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METHOD FOR DETERMINATION OF WATER IN BUTTEROIL BY NEAR-INFRARED SPECTROPHOTOMETRY

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ABSTRACT

A double beam near-infrared spectrophotometer has been used to quantitatively measure the amount of water in butteroil. For an analysis, the sample under investigation is dissolved in carbon tetrachloride, split, and one-half of the material dried by addition of calcium hydride. The difference in absorption at 1.9 μ between the moisture-containing portion and the dried portion of the sample is equated with the moisture content of the original sample.

By use of this relatively fast and accurate method, it was found that butteroil can be rapidly dried by contact with calcium hydride, anhydrous calcium chloride, and Linde Molecular Sieve 4A.[1] Water could also be removed from butteroil by vacuum drying of thin films of the material.

In water-saturated atmospheres butteroil absorbs water at a relatively rapid rate, dependent upon temperature.

It is becoming increasingly apparent that nonoxidative changes may occur in the fat phase of dairy products which influence their flavor. That changes of this type can occur in isolated milk fat has been demonstrated by the work of Tharp and Patton (15), Patton and Tharp (11), and Nawar (10). The role the water plays in promoting these reactions is subject to question. Nawar and others have suggested that methyl ketones are produced in heated fat in the absence of water, whereas recently Schwartz (12) and Langler (8) have obtained data showing that the presence of water is necessary for development of these materials in heated butteroil.

In the earlier papers (4-7, 14) the water content of the fat under investigation was not reported—possibly due to lack of a suitable method for determination of low levels of water in the presence of volatiles and material reacting nonspecifically with the Karl Fischer reagent. In view of our interest in factors influencing the flavor stability of dairy products, means for the determination of water in butteroil were studied.

This paper describes a nondestructive method for determination of the moisture content of butteroil. Also described is the effectiveness of the common methods of drying butteroil.

Our method of determining moisture in butteroil is based on the observation of other investigators (2, 9), that the intensity of the 1.9 μ near-infrared water absorption band can be equated with the water content of various organic solvents.

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[1] Reference to certain products or companies does not imply an endorsement by the Department over others not mentioned.

MATERIALS AND METHODS

The butteroil used in this work was obtained by melting unsalted butter churned from fresh, pasteurized sweet cream.

Molecular Sieve 4A was obtained from the Linde Air Reduction Company.[2] Spectral grade carbon tetrachloride was used as obtained from the Fisher Scientific Company.[2] All other chemicals were reagent grade chemicals, used as obtained from commercial supply houses.

A Perkin-Elmer Model 350 double beam recording spectrophotometer,[2] equipped with a lead sulfide detector and tungsten lamp source, was used to determine the absorption of near-infrared energy passing through 1 cm of sample contained in quartz cells.

The water content of butteroil was determined by observing the difference in absorption at 1.9 μ between the butteroil sample and an aliquot of this material from which all water had been removed by a drying agent. To facilitate the handling of butteroil at room temperature, two parts of all samples were diluted with one part of spectral grade carbon tetrachloride before further work was carried out.

Water-free samples of butteroil were prepared by using a mechanical wrist-action shaker oscillating at five cycles per minute to stir mix-

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tures in 125-ml glass-stoppered flasks containing 50 ml of butteroil solution and 1.5 g of calcium hydride for 3 hr. Preliminary observation of the absorption spectra in the vicinity of 1.9 μ showed this treatment sufficient to remove all detectable water. The suspended calcium hydride was removed from the dried material for spectrophotometric analysis and for preparation of a standard curve.

The standard curve was prepared by adding weighed amounts of water to known amounts of dried butteroil and equating the water content of the samples with the increased absorption observed at 1.9 μ. The absorbance of the water band was measured as the difference between the peak maximum near 1.9 μ and a horizontal base line, drawn from some reproducible point in the spectrum not affected by water concentration (1.1 μ).

All analyses were carried out in a room in which temperature was controlled at approximately 22 C. Using this general technique, the relative efficiency of various chemical and mechanical methods for removing water from butteroil was also determined.

Fifty-milliliter samples of butteroil in carbon tetrachloride were mechanically shaken, in uniform fashion, with 10-g portions of either anhydrous sodium sulphate or anhydrous calcium chloride or 1.5 g of calcium hydride. In similar fashion, 150-ml samples of butteroil solution were shaken with 60 g of Linde Molecular Sieve 4A.[2] During the shaking period samples were regularly withdrawn from the flask and their water content determined spectrophotometrically.

Physical methods commonly used for drying butteroil were tested by systematically determining the water content of a butteroil solution passing through a disc of Whatman no. 1 filter paper and of butteroil being dried under vacuum in a Rinco [2] rotating evaporator in which the 150-ml butteroil sample was filmed on the interior surface of a three-liter round-bottomed flask.

The relative rate of absorption of moisture by butteroil held at various temperatures was determined by placing 150-ml samples of mechanically dried butteroil in 4-in. Petri dishes and placing them in atmospheres saturated with water vapor at 40 and 100 C. Samples were withdrawn from these dishes at regular time intervals and their water content determined spectrophotometrically.

RESULTS

The spectrum obtained by recording the absorption difference between a moisture-containing butteroil sample and a moisture-free sample is shown in Figure 1. The height of the water absorption peak at 1.9 μ has been found to be directly proportional to the moisture content of the material in the sample beam of the spectrophotometer. The linearity of this plot over the range of 0 to 0.5% is shown in Figure 2.

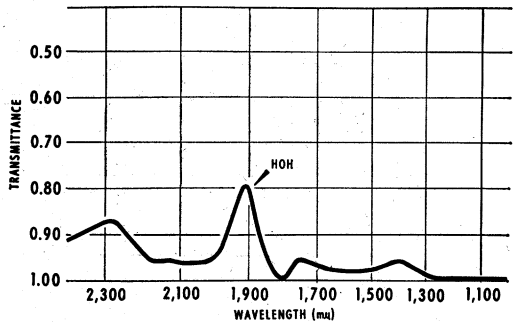

FIG. 1. Difference spectrum (wet/dry butteroil).

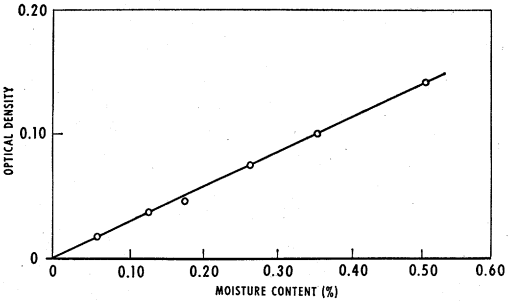

FIG. 2. Standard curve.

The relative efficiency of various common chemical drying agents used for removal of water from butteroil is shown in Figure 3. From this it can be seen that calcium hydride is a most efficient drying agent. Anhydrous sodium sulphate was found to be the poorest drying agent. Since calcium hydride was so

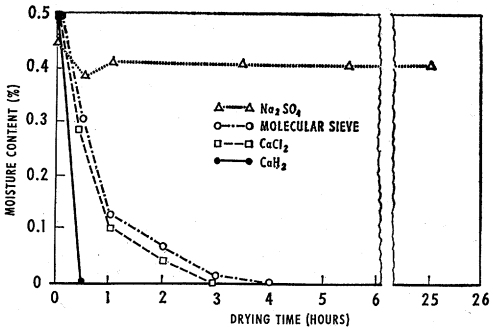

FIG. 3. Effect of various drying agents on the moisture content of butteroil.

rapid in its drying action, it was routinely used in our laboratory for the drying of samples to be used as reference material.

The passage of butteroil through a filter disc removed only a fraction of the water present in the oil. The first oil through the filter was most thoroughly dried, as would be expected. The general pattern of the change in water content of butteroil passing through a filter paper disc is shown in Figure 4.

The removal of water by vacuum drying of agitated films of butteroil is relatively efficient and at any temperature is pressure-dependent. This general effect is shown by the data presented in Figure 5.

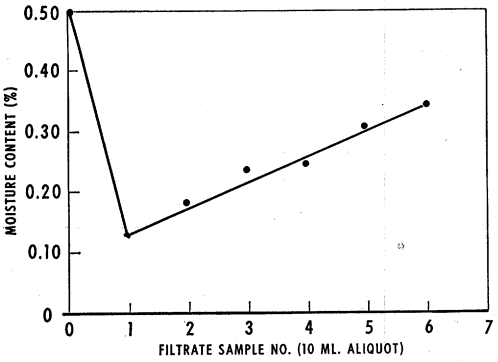

FIG. 4. Water removed from butteroil by passage through Whatman no. 1 filter paper.

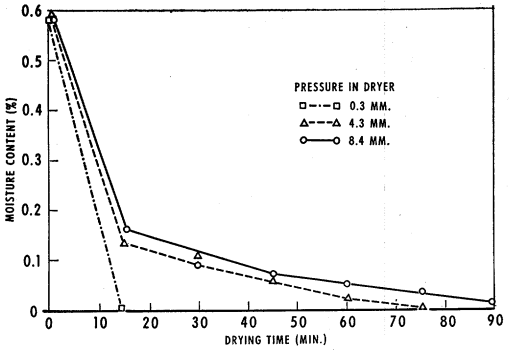

FIG. 5. Rate of drying butteroil under vacuum at 100 C.

The ability of butteroil to absorb water is shown by the data presented in Figure 6. Here it can be seen that butteroil in contact with atmospheres of relative humidities of 100% picks up water rather rapidly. The rate of water absorption is temperature-dependent and it is apparent that 1 hr of exposure of butteroil to a water-saturated atmosphere at 100 C is sufficient to bring the water content of the material above 0.5%. Even at 40 C an increase

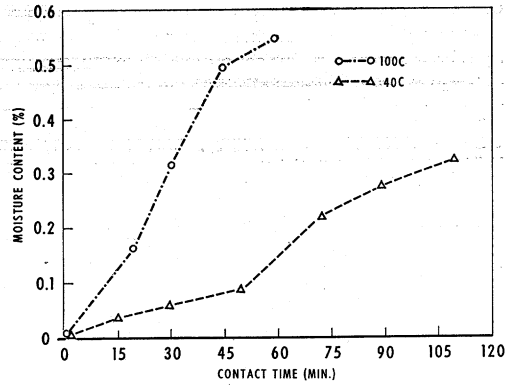

FIG. 6. Rate of absorption of moisture by butteroil in atmospheres of 100% R. H.

in the water content of the butteroil can be detected after 15 min of exposure to a water-saturated atmosphere.

DISCUSSION

The utility of near-infrared spectrophotometry as a means of determining the water content of butteroil is in agreement with previously published work describing the application of this method to the determination of water in various organic solvents (2, 3, 9, 13). These cited references indicate good agreement with the Karl Fischer titration method, where the latter is applicable.

Even though butteroil contains organic materials that absorb strongly in the vicinity of 1.9 μ, it is possible to determine the water absorption in this region by using a reference solution or blank consisting of a chemically dried sample of the oil under investigation.

The rapid and efficient drying action of calcium hydride in organic solvents as reported by Brown et al. (1) was also found to hold for the drying of butteroil. This hgih efficiency of calcium hydride in drying butteroil made the described method relatively rapid and accurate.

Actually, the most critical aspect of the spectrophotometric method is in the drying of the portion of the sample to be used in the reference beam of the spectrophotometer. Results will automatically be low by the amount of water not removed from the dried sample.

The sensitivity and accuracy of the method are also, at least in part, dependent upon the hydrogen-bonding properties of the material in the butteroil. The fact that butteroil contains some material that can form hydrogen bonds is perhaps the reason this method is less sensitive for detecting water in butteroil than in

other less polar systems. However, quantities of water in butteroil as low as 0.02% water can be detected with considerable accuracy by this method. The colloidal water found in butteroil in which water solubility limits are exceeded scatters radiation to some extent, and limits the use of this method in samples containing large amounts of colloidal water. However, as the standard curve indicates, the low level of scattering in the slightly hazy-appearing samples containing more than 0.3% water at room temperature (22 C) does not affect the linearity of the observed absorption.

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